Electronic Supplementary Information

Spin transition in a ferrous chloride complex supported by a pentapyridine ligand

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Experimental procedures

Synthesis of pyridine -2,6 -diylbis[di(pyridin -2 -yl)methanol] (Py5OH)



An excess amount of Mg was added to a dry THF (Tetrahydrofuran) solution (40 ml) of 2,6-Dibromopyridine (0.65 g, 2.72 mmol) in a 100 ml 3-neck round bottom flask. After sonicating the mixture for 20 minutes at 35°Cusing an ultrasonic bath (45 KHz frequency, model USC300TH, VWR Collection) the solution turned from transparent to black. This Grignard reagent was added dropwise into a dry THF solution (20 ml) of di(2-pyridyl)ketone (1.00 g, 5.44 mmol) with subsequent formation of a white precipitate. The reaction was monitored using HPLC-MS analysis ([Py5OH] H⁺= 448 m/z). After 48 hours, 30 ml of 10% HCl was added, the organic solvent was evaporated and the aqueous solution was washed with CH₂Cl₂ (2 × 50 mL). Neutralization of the aqueous solution with saturated Na₂CO₃ solution was followed by extraction with CH₂Cl₂ (3 × 100 mL). The solvent was evaporated and the penta-pyridylcarbinol product was recrystallized from hot acetone (250 mg, 0.558 mmol, 10.2% reaction yield). The following characterizations permitted us to verify the compound purity. ¹H-NMR (400 MHz, CDCl₃): δ = 7.17 (4 H, t of d, J₁ = 5.3 Hz, J₂ = 2.3 Hz, 5-H of Py arms (py-a)), 7.55-7.60 (8 H, m, 3-Hpy-a, 4-Hpy-a), 7.71 (3 H, m, 2-H and 3-H of bridging Py), 8.50 (4 H, m, 6-Hpy-a) ppm. ¹³C-NMR (400 MHz, CDCl₃): δ = 162.1, 161.2, 147.2, 137.8, 136.5, 123.5, 122.5, 120.8, 80.9 ppm. MS (⁺ESI-ToF): m/z: 448.1878 [Py5OH + H⁺]⁺, 470.1689 [Py5OH + Na⁺]⁺.

Synthesis of [Fe^{II}(Py5OH)Cl](PF₆)

The title was prepared as described previously with minor modifications.¹ All the reagents were kept under vacuum ($5 \cdot 10^{-4}$ bar) for 2 hours prior use. The synthetized Py5OH ligand (195.9 mg, 0.44 mmol) was dissolved in 25 mL of dry oxygen-free methanol in a 50 mL Schlenk flask tube. Subsequently, FeCl₂ (58 mg, 0.46 mmol, purity 98%) was introduced into the Schlenk flask tube under Argon counter flow. The solution changed color within 5 min of mild stirring at room temperature from yellow to orange. After 10 minutes an excess of KPF₆ (150 mg, 0.81 mmol) was added and after one hour of constant stirring yellow precipitate started to appear. The solid was collected employing Büchner filtration, washed with ca. 4 ml of cold mixture of methanol and water (4:1) and kept under vacuum overnight (140.8 mg, 0.21 mmol, 46.8% reaction yield). Elemental analysis for C₂₇H₂₁N₅O₂PCIF₆Fe: calcd. C, 47.43; H, 3.10; N, 10.24; found C, 47.61; H, 3.26; N, 10.09%.

Magnetic susceptibility measurements

Temperature dependent magnetic susceptibility measurements were carried out using a Quantum Design MPMS-XL-5 SQUID magnetometer equipped with a 7 T magnet over the temperature range 30–300 K with a heating and cooling rate of 2 K min⁻¹ and a magnetic field of 0.5 T. Diamagnetic correction for the molecule was derived from the Pascal's constants.

ESI mass spectrometry

Mass spectra were obtained using a micrOTOF-Q II TM ESI-Qq-TOF mass spectrometer (Bruker Daltonik GmBH, Billerica, Massachusetts, USA). The acetonitrile sample solution (approx. 0.5 mM)

was injected and the corresponding mass spectrograms were recorded over 60 seconds using the program MicrOTOFcontrol Version 3.0. Analysis and processing of the data was followed using the program DataAnalysis Version 4.0. High-resolution mass spectra were obtained with a standard deviation of 0.000442 m/z (Calibration mode: Enhanced Quadratic; Internal Score: 99.45 % with a 6-point calibration).

IR spectroscopy

FTIR-measurements were carried out using a Spectrum One FT-IR Spectrometer (Perkin Elmer Inc.) in transmission geometry in KBr pellets prepared using a hydraulic press (10 min, 10 tons). The spectrum (Figure S1) was obtained by averaging 32 scans with correction for atmospheric gases.

Powder X-ray diffraction

PXRD data was acquired at ambient temperature on a Bruker D5000 diffractometer using a copper anode ($\lambda = 1.5406$ Å) with a scan rate of 10 s per step with a step size of 0.05° in 2 Θ over the 2 Θ range of 5°–65°. The generator voltage was 45 kV and generator current was 40 mA.

Elemental analysis

Elemental analyses was performed with a 2400 Series II CHNS/O elemental analyzer (Perkin Elmer Inc.) operating in the CHN mode.

X-ray absorption spectroscopy

X-ray absorption spectroscopy measurements were performed at the KMC-3 beamline at the BESSY II synchrotron facility in Berlin, Germany. The incident X-ray energy was scanned through the Fe Kedge regions using a silicon (111) double-crystal monochromator. Measurements were performed with samples positioned at 45° with respect to the incident beam in a liquid helium cooled cryostat (Oxford Instruments). Samples were measured in powder form, mixed in ratio 1:30 with BN. A 10 um Fe foil (Goodfellow Cambridge Limited) positioned behind the sample served as calibration standard. Energy calibration was done by assigning the position of the maximum of the first derivative of the Fe foil absorption to 7112 eV. Iron Ka fluorescence signals from the sample were recorded with a 13-element silicon drift detector (RaySpec) positioned perpendicular to the incident beam. For each temperature, 8-16 scans were taken in the energy range from 7000 to 7860 eV, where each scan was pointed on a new sample spot, to avoid possible radiation damage; additionally, three consecutive scans at the same sample spot confirmed that there was no observable radiation damage on the time scale of the XAS measurement. EXAFS simulations were done with the FEFF 9.0 software⁶ (using settings NLEG 6, CRITERIA 12 5, RPATH 7, SCF 7 1 30 0.05). Least-squares fitting of k³-weighted EXAFS data by changing of interatomic distances for the first four single-scattering shells (see Table S1) and Debye-Waller factors for all shells (with all multiple-scattering shells having the same Debye-Waller factor) was done with SimXLite software, with fit parameter errors determined as described previously.⁷ The amplitude reduction factor S_0^2 was 0.85, E_0 used for EXAFS extraction was 7115 eV, and the k³-weighted EXAFS data was fitted between $k = 1.6 \text{ Å}^{-1}$ and 13 Å⁻¹. Parameters of EXAFS simulations are summarized in the Table S1.

Table S1. Iron-ligand distances (R / Å) and Debye-Waller factors (σ / Å) of shells used in the EXAFS simulations. Coordination numbers were fixed at values from the crystal structure. Numbers in parentheses show the uncertainty in the last digit corresponding to the 68% confidence interval of the fit parameter, obtained from the covariance matrix of the Levenberg-Marquardt fit. For the two Fe-C shells the same σ was used. Phase functions were generated by the FEFF9.0 software using the XRD structure (for 150 K and 293 K) or the LS DFT-geometry-optimized structure (for 20 K). Multiple-scattering shells (508 for 20 K, 862 for 150 K and 293 K) had the same σ , and R was not fitted.

		Fe–N	FeCl	Fe–C	Fe–C	Multiple-scattering
						shells
Coord	No	5	1	12	10	(multiple)
20 K	R	1.993(3)	2.378(6)	2.958(6)	4.25(3)	(multiple)
	σ	0.067(3)	0.050(6)	0.085(4)	0.085(4)	0.083(6)
150 K	R	2.178(6)	2.38(2)	3.094(6)	4.44(3)	(multiple)
	σ	0.070(4)	0.08(1)	0.081(5)	0.081(5)	0.084(6)
293 K	R	2.169(7)	2.39(2)	3.088(9)	4.44(6)	(multiple)
	σ	0.084(5)	0.09(1)	0.097(6)	0.097(6)	0.099(8)

Computational details

Density-functional theory (DFT) calculations were performed using Gaussian09 E.01.² All calculations were performed in a Polarizable Continuum Model (PCM) using the integral equation formalism (IEFPCM) with parameters for acetonitrile. All complexes were geometry optimized starting from their crystal structure using the B3LYP-D3 functional with the Lanl2TZ(f) basis set for iron, and 6-311+G(2df,2pd) for all other atoms.³ No internal instabilities could be detected after the self-consistent field (SCF) optimization. Hessian calculations were performed to ensure that all structures are minima on the potential energy surface. Thermal contributions are evaluated using the harmonic approximation based on force constants from a Hessian calculation. Relative spin-state energies were then calculated by varying the amount of HF exchange in the B3LYP functional down to 0% in steps of 5%-units. The relative energy of the singlet decreased almost linearly with decreasing percentage of HF exchange, with similar slopes for the two complexes, 1.27 kcal/mol for the title complex [Fe^{II}(Py5OH)Cl]⁺ and 1.25 kcal/mol for [Fe^{II}(Py5OMe)Cl]⁺ and [Fe^{II}(Py5OH)Br]⁺. To reproduce the experimentally observed spin-crossover temperature of 80 K for the title complex, B3LYP* (15% HF exchange) energies were further adjusted with an empirical correction of -1.56 kcal/mol for the singlet energy, which roughly corresponds to 14% HF exchange. The same empirical correction was then used for the singlet energy of the methoxy complex.

For the complex with the bromide ligand [Fe^{II}(Py5OH)Br]⁺, a small (-79 cm⁻¹) imaginary frequency was detected after optimization of the high-spin state and no lower-energy structure could be found even after distortions along this normal mode. The free-energy corrections for the bromide complex were instead evaluated against the chloride complex with the smaller Lanl2DZ basis set for iron and 6-31G(d,p) for the other atoms. Using a structure with an imaginary frequency slightly underestimates the stability of that state, but as the high-spin state is already stable, by 0.2 kcal/mol at 0 K, this does not affect the conclusions.

Atom coordinates of the optimized structures for $[Fe^{II}(Py5OH)CI]^+$, $[Fe^{II}(Py5OMe)CI]^+$ and $[Fe^{II}(Py5OH)Br]^+$ are summarized in the Table S2.



Figure S1. Powder X-ray diffraction (PXRD) of $[Fe^{II}(Py5OH)CI](PF_6)$ recorded at 293 K. The PXRD pattern simulated from the single crystal X-ray diffraction analysis of $[Fe^{II}(Py5OH)CI](PF_6)$ is shown as blue lines.¹ The relative intensities of Bragg reflections in the experimental and simulated PXRDs differ due to the preferential crystallographic orientation of the powder sample.



Figure S2. IR spectrum of $[Fe^{II}(Py5OH)CI](PF_6)$. Three moderate sharp peaks at 3102 cm⁻¹, 3060 cm⁻¹ and 3010 cm⁻¹ can be assigned to the v(CH) stretching modes of the ortho-substituted pyridines. The intense absorption band associated with the v(-C=C-C=) and v(-C=N-C=) stretching modes can be found around 1585 cm⁻¹. Further bands at 1435 cm⁻¹ suggest the existence of asymmetric, out-of-plane bending vibrations ω (CH). Typical symmetrical aromatic ring-breathing modes can be seen at 995 cm⁻¹ and 1052 cm⁻¹.⁴ Additionally, a strong out-of-plane bending mode δ (CH) can be observed at 756 cm⁻¹. These proposed assignments of the absorption bands are supported by theoretical and experimental IR spectra of pyridine and related pyridine derivatives.⁵ Bands at 852 cm⁻¹, 886 cm⁻¹ and 558 cm⁻¹ can be assigned to the stretching modes v(PF) and the bending mode δ (PF₆) of the hexafluorophosphate counter-ion present in the structure. Although all chemicals were dried overnight, water likely contaminated the sample during preparation of the KBr pellets, which appears as strong absorption around 3400 cm⁻¹. The bending modes δ (OH) of H₂O could also contribute to the strong absorption in the 1600 cm⁻¹ region.



Figure S3. High resolution mass spectra recorded in acetonitrile showing two main molecular fragments at m/z = 538.0894 and 502.1099, which correspond to $[Fe^{II}(Py5OH)CI]^+$ and $[Fe^{II}(Py5OH)-H]^+$ respectively. The fragment without chlorine ligand is generated by the ionization process as the ratio between intensities of both signals varies with the ionization intensity.



Figure S4. SCO curve of approx. 10mg of [Fe^{II}(Py5OH)Cl](PF₆) powder in the form of $\chi_M T vs T$ can be fitted using a thermal Boltzmann distribution (red line) indicating weak cooperativity of spin transition in the title complex.



Figure S5. EXAFS spectra of $[Fe^{II}(Py5OH)CI](PF_6)$ powder recorded at different temperatures. Simulations of the experimental data based on the molecular structure of the complex are shown as thin lines. Color code: 20 K, blue; 150 K, black; 293 K, red.

Table S2. XYZ coordinates of optimized structures. All geometries from B3LYP-D3 optimizations with the Lanl2TZ(f) basis set for iron and 6-311+G(2df,2pd) for all other atoms.

[Fe^{II}(Py5OH)Cl]⁺, LS state

E = -2	049.9875151		
Fe	0.000052	-0.000089	-0.701082
0	-3.496677	0.000056	2.094564
Н	-4.332551	0.000118	1.615570
Cl	0.000166	-0.000090	-3.088076
Ν	-0.000114	-0.000052	1.324931
Ν	1.517230	-1.363575	-0.653281
0	3.496320	0.000062	2.095120
Н	4.332267	0.000105	1.616256
Ν	1.517105	1.363488	-0.653312
Ν	-1.517104	-1.363608	-0.653474
Ν	-1.516987	1.363513	-0.653509
С	-1.621069	2.384861	-1.517657
Н	-0.922404	2.385316	-2.332590
С	1.621381	2.384789	-1.517492
Н	0.922890	2.385204	-2.332576
С	2.584753	3.371826	-1.415772
Н	2.608141	4.169937	-2.142389
С	3.494571	3.306083	-0.373998
Η	4.249163	4.068179	-0.241951
С	3.432920	2.223851	0.490905
Н	4.136232	2.136251	1.302261
С	2.452114	1.258814	0.306623
С	2.421743	0.000014	1.188807
С	1.149734	-0.000032	2.017060
С	1.192488	-0.000021	3.401833
Н	2.142927	-0.000002	3.906740
С	-0.000339	-0.000022	4.104591
Η	-0.000428	-0.000009	5.185115
С	-1.193052	-0.000021	3.401638
Н	-2.143573	-0.000002	3.906391
С	-1.150076	-0.000032	2.016872
С	-2.421958	0.000013	1.188419
С	-1.621372	-2.384916	-1.517651
Н	-0.922804	-2.385413	-2.332655
С	-2.584877	-3.371838	-1.416079
Н	-2.608245	-4.169950	-2.142694
С	-3.494876	-3.305961	-0.374473
Н	-4.249606	-4.067944	-0.242562
C	-3.433250	-2.223712	0.490404
H	-4.136717	-2.135987	1.301611
C	-2.452179	1.258817	0.306242
C	-2.584451	3.371904	-1.416091
H	-2.607676	4.170052	-2.142671
C	-3.494490	3.306117	-0.374512
H	-4.249108	4.068209	-0.242591
С	-3.433018	2.223853	0.490362

Н	-4.136493	2.136233	1.301574
С	2.452221	-1.258801	0.306660
С	3.433145	-2.223716	0.490956
Н	4.136441	-2.136020	1.302315
С	3.494951	-3.305931	-0.373952
Н	4.249647	-4.067924	-0.241909
С	2.585184	-3.371754	-1.415763
Н	2.608718	-4.169825	-2.142418
С	1.621694	-2.384833	-1.517493
Н	0.923309	-2.385280	-2.332656
С	-2.452285	-1.258806	0.306277

[Fe^{II}(Py5OH)Cl]⁺, HS state

E= -2049.99390889

Fe	0.000007	0.000030	-0.965045
0	3.503429	-0.000115	2.132025
Н	4.352997	-0.000135	1.677970
Cl	0.000023	0.000132	-3.321871
Ν	-0.000010	-0.000061	1.326719
Ν	-1.660979	1.422893	-0.679871
0	-3.503462	-0.000063	2.131967
Н	-4.353023	0.000013	1.677899
Ν	-1.660927	-1.422911	-0.679936
Ν	1.660934	1.422956	-0.679794
Ν	1.660994	-1.422846	-0.679955
С	1.762190	-2.485843	-1.486786
Н	1.063226	-2.520407	-2.307554
С	-1.762073	-2.485927	-1.486748
Н	-1.063057	-2.520514	-2.307469
С	-2.709304	-3.478205	-1.309097
Н	-2.749605	-4.316243	-1.988517
С	-3.582242	-3.364179	-0.238124
Н	-4.324399	-4.125789	-0.045223
С	-3.499091	-2.250374	0.586022
Н	-4.167502	-2.148901	1.424650
С	-2.537122	-1.280451	0.322327
С	-2.456997	-0.000061	1.187819
С	-1.155509	-0.000095	2.003872
С	-1.196715	-0.000156	3.391376
Н	-2.141793	-0.000180	3.905546
С	-0.000032	-0.000186	4.088484
Н	-0.000041	-0.000235	5.169322
С	1.196662	-0.000152	3.391395
Н	2.141731	-0.000173	3.905581
С	1.155479	-0.000087	2.003891
С	2.456980	-0.000038	1.187860
С	1.762081	2.486040	-1.486516
Н	1.063089	2.520678	-2.307255
С	2.709285	3.478324	-1.308755
Η	2.749588	4.316418	-1.988104
С	3.582192	3.364230	-0.237763

Η	4.324326	4.125842	-0.044776
С	3.499042	2.250353	0.586288
Н	4.167430	2.148826	1.424928
С	2.537130	-1.280410	0.322359
С	2.709411	-3.478124	-1.309096
Н	2.749757	-4.316145	-1.988533
С	3.582287	-3.364120	-0.238068
Н	4.324436	-4.125732	-0.045140
С	3.499090	-2.250328	0.586091
Н	4.167461	-2.148852	1.424754
С	-2.537119	1.280390	0.322431
С	-3.499055	2.250309	0.586248
Н	-4.167426	2.148778	1.424904
С	-3.582228	3.364172	-0.237817
Н	-4.324358	4.125785	-0.044824
С	-2.709354	3.478245	-1.308840
Н	-2.749683	4.316323	-1.988208
С	-1.762154	2.485958	-1.486614
Н	-1.063192	2.520573	-2.307380
С	2.537104	1.280430	0.322481

[Fe^{II}(Py5OMe)Cl]⁺, LS state

E= -2	2128.59766860)	
Fe	-0.000008	0.284653	-0.729038
Cl	0.000051	0.981280	-3.015756
0	3.564402	-0.611418	1.841047
0	-3.564334	-0.611450	1.841127
Ν	0.000018	-0.370122	1.140716
Ν	1.511404	1.557744	-0.276520
Ν	1.567390	-1.049201	-1.126453
Ν	-1.567408	-1.049189	-1.126443
Ν	-1.511462	1.557704	-0.276575
С	1.155317	-0.744083	1.710843
С	1.190366	-1.614577	2.790074
С	0.000048	-2.069013	3.326631
С	-1.190286	-1.614586	2.790101
С	-1.155262	-0.744094	1.710868
С	2.455368	-0.324156	1.025358
С	3.669337	0.043877	3.118869
С	2.508609	1.128733	0.517304
С	3.643778	1.898507	0.743632
С	3.742467	3.163598	0.188317
С	2.712709	3.609365	-0.621638
С	1.638751	2.768784	-0.842126
С	2.558708	-1.201122	-0.228251
С	3.625088	-2.065605	-0.417263
С	3.689521	-2.803216	-1.590109
С	2.695421	-2.626799	-2.539313
С	1.667629	-1.739317	-2.272004
С	-2.455324	-0.324172	1.025413

С	-3.669208	0.043796	3.118979
С	-2.558692	-1.201129	-0.228205
С	-3.625075	-2.065612	-0.417195
С	-3.689557	-2.803191	-1.590059
С	-2.695505	-2.626736	-2.539307
С	-1.667702	-1.739261	-2.272016
С	-2.508596	1.128719	0.517355
С	-3.643749	1.898496	0.743750
С	-3.742512	3.163548	0.188360
С	-2.712859	3.609261	-0.621759
С	-1.638907	2.768685	-0.842290
Η	2.131365	-1.968003	3.170439
Η	0.000060	-2.774300	4.144949
Η	-2.131275	-1.968017	3.170486
Η	3.615036	-0.700943	3.909931
Н	4.637655	0.536786	3.171494
Н	4.458819	1.504118	1.321075
Η	4.618249	3.770805	0.367081
Η	2.742643	4.573507	-1.106328
Η	0.874824	3.048702	-1.539336
Н	4.384397	-2.144459	0.342321
Н	4.507987	-3.487904	-1.761397
Η	2.709382	-3.155282	-3.480636
Н	0.913905	-1.542108	-3.010089
Η	-3.614852	-0.701053	3.910010
Η	-4.637531	0.536687	3.171676
Н	-2.883613	0.781810	3.271139
Н	-4.384352	-2.144489	0.342419
Н	-4.508027	-3.487878	-1.761329
Н	-2.709512	-3.155183	-3.480649
Н	-0.914016	-1.542014	-3.010131
Н	-4.458731	1.504138	1.321297
Н	-4.618280	3.770758	0.367181
Η	-2.742873	4.573355	-1.106539
Η	-0.875079	3.048535	-1.539640
Η	2.883740	0.781886	3.271045

Fe^{II}(Py5OMe)Cl]⁺, HS state

E= -2	2128.60847383		
Fe	-0.000034	0.352363	-0.937786
Cl	-0.000470	1.006778	-3.194169
0	3.550024	-0.590767	1.938642
0	-3.551101	-0.591090	1.936961
Ν	-0.000312	-0.317905	1.175934
Ν	1.631121	1.639151	-0.229513
Ν	1.748485	-1.108108	-1.135921
Ν	-1.749130	-1.106120	-1.137640
Ν	-1.629042	1.641063	-0.225953
С	1.158436	-0.789223	1.654351
С	1.193053	-1.824017	2.581105

С	-0.000745	-2.350806	3.040411
С	-1.194341	-1.824144	2.580413
С	-1.159316	-0.789328	1.653709
Ċ	2 494551	-0.312555	1 046841
C	3 513633	0.035016	3 232564
C	2 595212	1 153454	0 562792
C	2.373212	1 880640	0.826263
C	2 00000	2 164209	0.820203
C	3.880098	3.104208	0.297231
C	2.870590	3.667790	-0.508648
C	1.//4/46	2.862331	-0./55401
C	2.707959	-1.188697	-0.203683
С	3.824548	-1.998095	-0.350413
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Fe^{II}(Py5OH)Br]⁺, HS state

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С	-2.532716	-1.282979	0.541488

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